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YEAR-ROUND MEASUREMENTS OF OZONE AT 66°S WITH A VISIBLE SPECTROMETER.

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1. INTRODUCTION

In March 1990, a zenith-sky UV-visible spectrometer of the design "Systeme Automatique d'Obervation Zenithal" (SAOZ, Pommereau & Goutail 1988) was installed at Faraday in Antarctica (66.3°S, 64.3°W). SAOZ records spectra between 290 and 600 nm during daylight. Its analysis program fits laboratory spectra of constituents, at various wavelengths, to the differential of the ratio of the observed spectrum and a reference spectrum. The least-squares fitting procedure minimises the sum-of-squares of residuals. Ozone is deduced from absorption in its visible bands between 500 and 560 nm.

The fortunate co-location of this SAOZ with the well-calibrated Dobson at Faraday has allowed us to examine the calibration of the zero of the SAOZ, difficult at visible wavelengths because of the small depth of absorption. Here we describe recent improvements and limitations to this calibration, and discuss SAOZ measurements of ozone during winter in this important location at the edge of the Antarctic vortex.

2. CALIBRATION

The outputs from the analysis program (differences in line-of-sight amounts between measured and reference spectra) have an offset equal to the amount in the reference spectrum, plus the amount due to instrumental artifacts which correlate with the ozone spectrum. Correlations are greater for measurements of ozone at visible than at UV wavelengths because the visible absorption cross-sections are much smaller.

We investigated offsets by plotting the analysed amounts against air-mass factors and extrapolating to zero air-mass (Langley plots). Fig. 1 shows the intercepts of all these plots, equal to the offsets, whose variability was increased by a hardware fault, now repaired. Nevertheless, much of the variability demonstrates the difficulties of Langley plots of zenith-sky data at high latitude: extra light is reflected from snow on the ground at high sun; the range of air-mass factors is restricted in winter; and snow showers cause extra scattering which greatly increases the line-of-sight amounts of the interfering constituents O_4, H_2O and ice.

To avoid these difficulties, we filtered the data by fitting a simple formula to the statistical errors and using it to reject noisy data; and by rejecting days whose maximum fluxes at 550 nm exceeded a smooth curve through the fluxes. The offsets from Langley plots of filtered data in Fig. 2 are much more plausible than those from unfiltered data in Fig. 1.

We investigated possible causes of the significant drift in Fig. 2. Offsets correlated with wavelength shifts between the measurement of the spectrum and the acquisition of the reference spectrum. This is consistent with the obvious physical model: if sensitivities of adjacent detector pixels differ, and if these differences correlate with the spectrum of ozone, there will be an instrumental offset; if the wavelengths of the pixels change, so will the degree of correlation and so the amount of the offset. Offsets were also correlated with temperature but not independently of wavelength shift.

Offsets from filtered data could not be used to calculate daily ozone because many days had been removed. We investigated several methods of interpolation - a straight-line fit to the offsets, several smoothing functions which were later discarded because of arbitrary assumptions in their formulation, and offsets calculated from a straight-line fit to wavelength shifts.

Fig. 2 shows that offsets calculated from wavelength shifts agree with the observed offsets better than the straight line. Table 1 shows that the standard deviation of the ratio of Dobson to SAOZ measurements was smaller using offets calculated from wavelength shifts, another indicator of a better approach. However, a true physical model would require measurement of the relative responsivities of each pixel of the detector, using a tungsten lamp. The resulting change of offset with wavelength shift would be a cyclic function rather than a straight line.

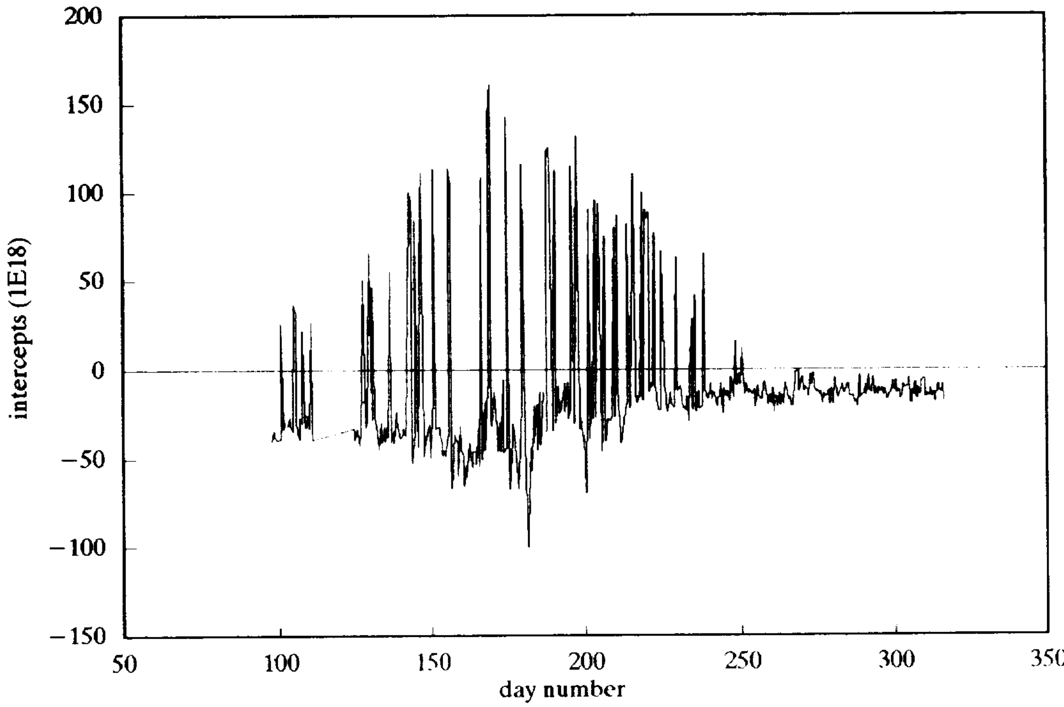

Fig. 1. Intercepts (offsets) from Langley plots of half-day's data. Note the large scatter, discussed in the text (10×10^{18} molec cm^{-2} is 370 DU).

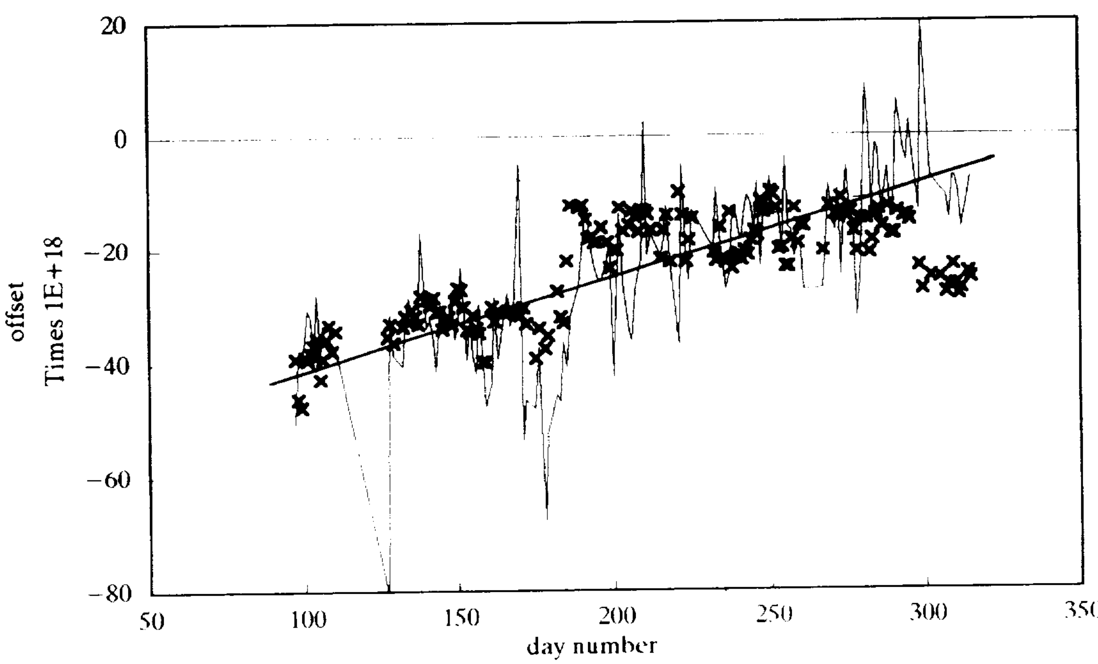

Fig. 2. Offsets from Langley plots of filtered data (thin line), a straight-line fit (thick line), and offsets calculated from a fit between wavelength shifts and measured offsets (points).

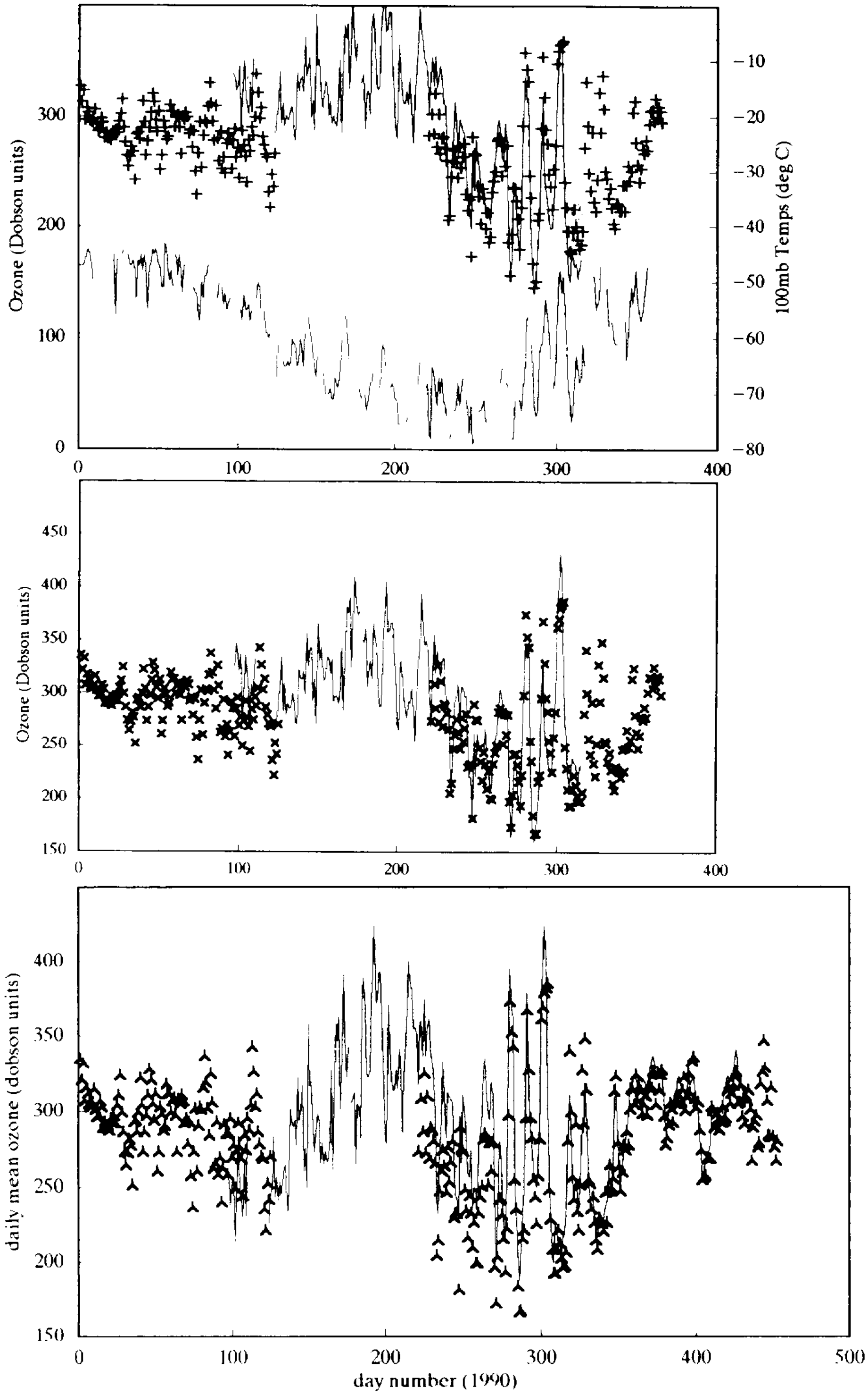

Fig. 3. Daily ozone from SAOZ at Faraday in 1990 (line), compared to ozone from the Dobson at Faraday (points, courtesy J.D.Shanklin). The extra coverage by SAOZ in winter is due to its use of visible rather than UV wavelengths. SAOZ offsets are from (a) the straight line in Fig. 2; (b) wavelength shifts with data to Nov 1990, (c) wavelength shifts with data to Feb 1991. The lower trace in (a) is 100 mbar temperatures at Bellingshausen, north of Faraday, whose correlations with ozone during winter show when air above the site is outside rather than inside the vortex.

Other SAOZ instruments do not show such a large trend in offsets. This is probably because the wavelength shift in SAOZ at Faraday is large, about 5 nm, perhaps due to vibration during shipping, and because the periodicity of the visible ozone spectrum is about 20 nm. Nevertheless, the methodology necessary to improve SAOZ at Faraday would improve others.

Table 1 also defines the relative error - the sum of systematic errors which are specific to one instrument and exclude absolute errors in laboratory cross-sections - to be ±10%, and the absolute error relative to the Dobson to be 3%.

3. RESULTS

Fig. 3 demonstrates the overwhelming advantage of zenith-sky measurements of visible ozone in such a cloudy place as Faraday at high latitude - measurements are now available throughout the winter. Dobson measurements during the three months of winter are only available on rare nights with clear moonlit periods, because the sun is so close to the horizon that the intensity of the direct sun is too low at the UV wavelengths used, and because zenith-sky measurements in the UV miss the lower part of the ozone column. Furthermore, Dobson observations of the direct moon require considerable operator skill.

Unfortunately, the winter trends in Fig. 3 depend on the method of determining offsets. The straight-line fit (Fig. 3a) gives a small rising trend outside the vortex, and almost no trend inside. The calculation from wavelength shifts using data to Nov 1990 (Fig. 3b) gives rising trends inside and outside the vortex in the early winter, followed by falls in ozone later in the winter. The similar calculation using data to Feb 1991 (Fig. 3c) showed a similar rise then fall outside the vortex but a steady rise inside. Clearly lamp measurements to determine offsets are needed before we can make definitive statements about the trend.

TABLE 1. *Mean and standard deviation of the ratio of the vertical column of ozone at Faraday from the Dobson, to that derived from SAOZ data*

method of determining offset	straight-line fit to measured offsets	calculated from wavelength shift
mean	1.034	0.971
standard deviation	0.145	0.102

However, from this preliminary analysis, ozone increased during the early part of the winter, both inside and outside the vortex. The rise outside the vortex is that expected from continued poleward and downward transport of air from the sub-tropics. The rise inside the vortex indicates descent early in the winter. Satellite measurements by TOMS do not cover this period close to the terminator with sufficient accuracy to determine a winter trend, but measurements at Halley before the ozone hole appeared showed approximately the same ozone entering as exiting the winter night (Farman, pri.com).

REFERENCES

Pommereau, J-P. and F. Goutail, Stratospheric O_3 and NO_2 observations at the southern polar circle in summer and fall 1988, *Geophys. Res. Lett.* 15, 895-897 (1988).